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**WO 01/76735 A1**

(54) Title: PROCESS FOR PREPARING FISCHER-TROPSCH CATALYST

(57) Abstract: Disclosed herein is a process for preparing a Fischer-Tropsch catalyst. The process comprises the steps of: impregnating a particulate carrier with an active metal selected from cobalt, iron, manganese, and nickel by mixing the particulate carrier with a particulate active metal compound at a temperature approximately at or above the melting point of the active metal compound but below the temperature at which such compound decomposes; and then calcining the thus impregnated carrier to produce the catalyst.

## PROCESS FOR PREPARING FISCHER-TROPSCH CATALYST

### BACKGROUND OF THE INVENTION

5           This invention relates to Fischer-Tropsch catalysts, and more particularly to a process for preparing a Fischer-Tropsch catalyst.

          Synthesis gas (typically a mixture of carbon monoxide and hydrogen) can be converted into hydrocarbons in the presence of a Fischer-Tropsch catalyst under suitable pressure and temperature conditions. The Fischer-Tropsch catalyst is typically comprised of a particulate carrier  
10           impregnated with an active metal, particularly cobalt, iron, manganese, or nickel. In preparing such a catalyst, impregnation is commonly carried out by using a compound of the active metal in aqueous solution.

## SUMMARY OF THE INVENTION

The invention provides a novel process for preparing a Fischer-Tropsch catalyst comprising the steps of: impregnating a particulate carrier with an active metal selected from cobalt, iron, manganese, nickel and mixtures thereof by mixing the particulate carrier with a particulate compound of  
5 containing said active metal at a temperature approximately at or above the melting point of the active metal compound but below the temperature at which such compound decomposes; and then calcining the thus impregnated carrier to produce the catalyst.

10 As demonstrated in the subsequent examples, the process of the invention produces a Fischer-Tropsch catalyst in which there is substantial penetration of the active metal in the carrier particles. As compared to a more typical profile in which the active metal is concentrated on the outer surfaces of the carrier particles, active metal penetration as achieved by the inventive  
15 process will generally enhance selectivity and/or activity, and will also minimize attrition or loss of active metal from the carrier particles and consequent contamination of the hydrocarbon product.

## DETAILED DESCRIPTION OF THE INVENTION

Now describing preferred details of the inventive process, the particulate carrier can be an oxide of silicon, aluminum, titanium, zinc, zirconium, or magnesium; zeolites; or a mixture thereof. Alumina is most preferred.

The active metal compound preferably has an active metal selected from cobalt, iron, manganese, nickel and mixtures thereof. Suitable active metal compounds include halides, nitrates, sulfates, acetates and thiocyanates of the active metal. The active metal compound preferably has a melting point in the range of about 25-400°C, most preferably about 25-100°C. Falling within the latter most preferred range are, for example, cobalt(II) bromide hexahydrate, cobalt(II) chlorate hexahydrate, cobalt(II) nitrate hexahydrate, cobalt(II) acetate, dicobalt octacarbonyl, cobalt palmitate, cobalt(II) sulfate heptahydrate, iron(III) chloride hexahydrate, iron(II) nitrate hexahydrate, iron(II) sulfate heptahydrate, nickel(II) nitrate hexahydrate, nickel(II) sulfate heptahydrate, nickel(II) sulfate hexahydrate, manganese(II) chloride tetrahydrate, and manganese(II) nitrate tetrahydrate. The most preferred active metal is cobalt, and the most preferred cobalt compound is cobalt(II) nitrate hexahydrate.

Any suitable means can be used to mix the particulate carrier and the particulate active metal compound. The inclined rotary apparatus used in a subsequent example has been found to be an effective mixing means. As indicated previously, the mixing is carried out at a temperature approximately at or above the melting point of the active metal compound but below the temperature at which such compound decomposes. By way of example, the mixing temperature for cobalt(II) nitrate hexahydrate is preferably in the range of about 55-170°C, most preferably about 60-130°C. The required time for mixing is typically less than 1 hour, most typically about 15-30 minutes. By such procedure, the particulate carrier is impregnated with the active metal compound.

If the active metal compound is a hydrate and loses water of hydration during impregnation, the impregnated carrier is preferably dried in flowing air at a temperature of about 60-120°C for a time of about 0.1-4 hours. The impregnated carrier is then calcined at a suitable temperature, typically in the range of about 200-800°C. Calcination is preferably carried out in a flowing air environment for a time of about 0.5-8 hours.

Optionally, the particulate carrier can be impregnated with a promoter metal to enhance the catalytic activity or to modify its selectivity. Useful promoter metals are potassium, chromium, magnesium, zirconium,

ruthenium, thorium, hafnium cerium, rhenium, uranium, vanadium, titanium, manganese, nickel, molybdenum, wolfram, lanthanum, palladium, praseodymium, neodymium or other elements from groups IA or IIA of the periodic table of the elements. Preferred promoters are selected from platinum, rhodium, ruthenium, and palladium. Platinum is most preferred. Any suitable means can be used to impregnate the particulate carrier with the promoter metal. Impregnation of the particulate carrier with the promoter metals is typically carried out by using a promoter metal containing compound. Suitable compounds include halides, nitrates, sulfates, acetates and thiocyanates of the promoter metal. Preferably the metal promoter containing compound will be soluble in water. According to an incipient wetness technique, the particulate carrier can be sprayed with an impregnation solution, having a suitable promoter metal compound dissolved in water or other solvent, while agitating the particulate carrier with the above-mentioned inclined rotary apparatus. Alternatively, slurry impregnation could be employed. The particulate carrier, as now impregnated with a promoter metal as well as the active metal, is again dried and calcined, substantially as described above.

The active metal in the finished catalyst can be, by way of example, in the range of about 1-30 wt.%. The promoter metal in the catalyst can be in the range of about 0.01-5 wt.%. Weight percentages are based upon

the total weight of the catalyst. If desired, the particulate carrier could also be impregnated with a carrier stabilizer such as barium or lanthanum.

All steps of the inventive process can be conveniently carried out at atmospheric pressure; as was the case in the inventive examples which are described below to further illustrate the invention. These examples should not be construed to limit the invention in any manner.

## EXAMPLES

### A. Example I

A particulate alumina carrier (obtained from Condea Chemie, Hamburg, Germany, under the designation "Pural SCF") was first heated in a muffle furnace at 750°C for 16 hours. After cooling, a sample was analyzed and found to have a surface area of 148 m<sup>2</sup>/g. 50.0 g of the alumina was placed in a beaker and heated in an oven to 121°C (250°F). The beaker was then placed on an inclined rotary apparatus. While such apparatus rotated the beaker, 67.5 g of powdered (250-325 mesh) cobalt(II) nitrate hexahydrate was gradually sprinkled into the beaker to thereby mix with the alumina. The beaker contents were kept hot by using a hot air gun. This procedure was continued until there was a uniform coating of the cobalt compound on the alumina particles. Alumina impregnated with the cobalt compound results.

The thus impregnated alumina was loaded into a 2 inch diameter quartz tube. After starting a flow of air through the tube at 80 cc/min, the temperature of the tube and its contents was ramped from ambient temperature to 80°C at 3°C/min. The temperature was held at 80°C for 2 hours. After cooling to ambient temperature, air flow was reset at 300 cc/min. The temperature was ramped to 240°C at 3°C/min, and held at 240°C for 2 hours. The cobalt impregnated alumina was allowed to cool, and then transferred from the quartz tube to a beaker.

1.4 g of tetra ammine platinum nitrate solution (containing 2.0 wt.% platinum) was diluted in 20.0 ml of distilled water to produce an aqueous solution. While rotating the beaker with the inclined rotary apparatus, an ultrasonic atomizer was used to spray the aqueous solution onto the cobalt impregnated alumina particles. The alumina, as now impregnated with platinum as well as cobalt, was heated in flowing air at 100°C for 2 hours and then at 240°C for 2 hours in a manner substantially similar to that described above, thereby resulting in the finished catalyst (Catalyst A).

Scanning Electron Microprobe analysis was performed on particles of the catalyst. The weight percentage of cobalt was measured at 2.0 micron increments, starting at the edge (0.0) and ending at an increment close to the center of the particle. Platinum was not measured. The following table

provides data for nine particles (where "P" stands for "Particle"). This data clearly shows the effectiveness of the inventive process in achieving cobalt penetration in the particles.

Cobalt (wt.%)

5	P	0.0	2.0	4.0	6.0	8.0	10.0	12.0	14.0	16.0	18.0	20.0	22.0
	1	18.7	18.9	15.4	21.6	12.6	14.7						
	2	0.5	2.7	15.7	10.0	8.7	5.7						
	3	0.2	0.5	20.4	12.7	5.3	4.0	6.7	8.2	12.0			
	4	1.5	2.3	14.2	4.0	0.8	1.7	4.9					
10	5	12.1	19.1	6.3	1.3	2.1	4.5	11.7	9.7	7.9			
	6	10.1	4.5	3.7	0.8	1.1	0.9	1.1	0.9	0.9			
	7	10.5	5.4	4.5	3.5	6.8	11.3	8.4	6.2	6.5	4.6	3.1	2.3
	8	10.6	12.2	14.2	15.2	15.3	13.5						
	9	28.7	11.7	10.0	4.5	0.8	1.7	0.8	1.2	0.3	0.3	0.2	

15      B.      Control I

A Catalyst was prepared in accordance with the process described in US 5,733,839. 50 g of alumina carrier (obtained from Condea Chemie, Hamburg, Germany, under the designation "Puralox SCCa") was added to a solution of 40.0 g of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  dissolved in 50 ml distilled water. The resultant slurry was treated for 2.5 hours at 75°C and 3.4 kPa in a rotary evaporator to impregnate the alumina carrier and to dry the impregnated carrier.

The dried impregnated carrier was calcined at 230°C for 2 hours in an air flow of 1.5 l<sub>n</sub>/min. The resultant calcined sample was re-slurried in a solution that was made up by dissolving 35.0 g Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and 53 mg Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> in 50 ml of distilled water. This slurry was again vacuum treated for 2.5 hours at 75°C and 3.4 kPa until free flowing in rotary evaporator. The dried impregnated carrier was calcined at 230°C for 2 hours in an air flow of 1.5 l<sub>n</sub>/min to produce the finished catalyst (Catalyst B).

#### C. Control II

A particulate alumina carrier (obtained from Condea Chemie, Hamburg, Germany, under the designation "Puralox SCCa") was first heated in a muffle furnace at 120°C for 4 hours. After cooling, 50.0g of the alumina was placed in a beaker. An aqueous solution was prepared containing 70g of water, 75 g Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, and 0.68 g of a platinum chloride (10 wt.%) solution (containing from 3.6 to 4.0 wt.% platinum). 90g of this solution was added to the beaker containing the alumina and stirred at room temperature for 1 hour. The mixture was next heated on a hot plate to dryness while stirring. The resulting material was further dried overnight in air at a temperature of 120°C followed by calcining at a temperature of 350°C for 3 hours. After cooling to room temperature the resulting material was further impregnated with the

remaining solution (55.68g) using the same procedure to produce the finished catalyst (Catalyst C).

#### D. Catalyst Test Procedure

The reactor used in this catalyst test was a 300 cc stirred tank reactor (purchased from Autoclave Engineers). For each catalyst tested, 10 grams of catalyst were loaded into the reactor and reduced with pure hydrogen at 300°C, atmospheric pressure and 100 cc/min of hydrogen for approximately 6 hours with slow stirring. After the hydrogen reduction, the catalyst was cooled to room temperature in hydrogen atmospheric environment. After cooling, approximately 90 g of octadecane were injected into the reactor. Then the system was pressurized to 300 psig with a mixture of CO and H<sub>2</sub> and the temperature increased to 220°C for reaction. The feed gas (CO and H<sub>2</sub>) flow rate and feed ratio were controlled using two calibrated mass flow controllers. The stirring speed was maintained at 1200 rpm during all tests, which was sufficient to minimize mass transfer effects between the gas and slurry phases. The exit gas from the reactor passed through a high-pressure trap (same pressure as the reaction), then to a low-pressure ice trap (atmospheric pressure) to collect the liquid products. The outlet gas was sent to an on-line gas

chromatograph for compositional analysis. A wet test meter was used to measure the flow rate of the outlet gas. The tests were conducted for three days. The liquid product was measured and analyzed everyday. At the end of the run, the mixture of catalyst, octadecane and wax product accumulated in the reactor was discharged from the reactor. The catalyst was separated by hot filtration through a Whatmans 42 filter paper. The wax mixture was analyzed by gas chromatography. The final product distribution was determined by combining gas phase, liquid product from the two condensers, and product in the octadecane solvent. The results for each catalyst are shown in Table I.

TABLE I

Catalyst	Catalyst A	Catalyst B <sup>1</sup>	Catalyst C
Day 1 run			
CO conversion (%)	25.08	31.33	25.49
Selectivity to HC	96.87	95.63	94.70
Selectivity to CO <sub>2</sub>	3.13	4.37	5.30
Day 2 run			
CO conversion (%)	25.13	30.84	32.37
Selectivity to HC	97.95	96.40	96.56
Selectivity to CO <sub>2</sub>	2.05	3.60	3.44
Day 3 run			
CO conversion (%)	19.88	28.00	22.69
Selectivity to HC	97.61	96.86	99.19
Selectivity to CO <sub>2</sub>	2.39	3.14	0.81

5

10

TABLE I (Cont.)

Catalyst	Catalyst A	Catalyst B <sup>1</sup>	Catalyst C
Product distribution (wt%)	Olefin to paraffin ratio	Olefin to paraffin ratio	Olefin to paraffin ratio
C1	9.47	9.45	10.25
C2-C4	8.75	10.28	10.47
C5-C11	20.90	23.64	27.59
C12-C18	19.65	22.95	20.97
C19+	41.23	33.70	30.72
Co Content <sup>2</sup> (ppm)	4.0	13.3	1.9

<sup>1</sup> The data for Catalyst B is an average of two runs except for the Co content where only one of the two runs was analyzed for Co content.

<sup>2</sup> Cobalt content of the wax product and solvent measured using x-ray fluorescence.

The results from Table I indicate that the inventive method of producing a Fischer-Tropsch catalyst results in a catalyst with favorable selectivity, conversion and product distribution. The low Co content for Catalyst A illustrates that the catalyst has a low attrition even using calcining temperatures that are relatively low. (Note Catalyst A used a calcining temperature of 240°C and Catalyst C used a calcining temperature of 350°C).

Additionally, experiments with other catalyst preparation methods have indicated that Puralox SCCa alumina may result in better carbon monoxide conversion and a more attrition-resistant catalyst than Pural SCF alumina.

Accordingly, it is believed that a catalyst made in accordance with the inventive process and using Puralox SCCa alumina would result in an better catalyst than Catalyst A.

Obviously, many modifications and variations of the present invention are possible in light of the above teachings. It is, therefore, to be understood that the invention may be practiced otherwise than as specifically described.

## THAT WHICH IS CLAIMED IS:

1. A process for preparing a Fischer-Tropsch catalyst comprising the steps of:

impregnating a particulate carrier with an active metal by mixing the particulate carrier with a compound containing the active metal at a temperature approximately at or above the melting point of the compound but below the temperature at which such compound decomposes to produce an impregnated carrier.

2. A process according to claim 1 wherein after impregnation with the active metal, the impregnated carrier is calcined.

3. A process according to claim 1 wherein the active metal is selected from cobalt, iron, manganese, nickel and mixtures thereof.

4. A process according to claim 3 wherein the active metal is cobalt.

5. A process according to claim 1 further comprising impregnating the impregnated carrier with a promoter.

6. A process according to claim 5 wherein said promoter is selected from platinum, rhodium and palladium.

7. A process according to claim 6 wherein the promoter is platinum.

8. A process according to claim 1 where in the compound is a particulate compound.

9. A process for preparing a Fischer-Tropsch catalyst comprising the steps of:

impregnating a particulate carrier with cobalt by mixing the particulate carrier with a particulate cobalt compound at a temperature approximately at or above the melting point of the compound but below the temperature at which such compound decomposes to produce an impregnated carrier;

calcining the impregnated carrier to produce a calcined impregnated carrier; and

impregnating the calcined impregnated carrier with a platinum compound to produce the catalyst.

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US00/10520

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : B01J 23/40, 23/42, 23/44, 23/72, 23/74, 23/75

US CL : 502/326, 337, 338, 339

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 502/326, 337, 338, 339

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,981,608 A (GEERLINGS et al) 9 November 1999 (09.11.1999), columns 3-6.	1-9
X	US 4,209,424 A (LE GOFF et al) 24 June 1980 (24.06.1980), columns 9-10, Example 12.	1-3, 8
X	US 5,008,234 A (OZIN et al) 16 April 1991 (16.04.1991), columns 3-7.	1, 3-8
X	US 5,714,092 A (VAN LOOIJ et al) 03 February 1998 (03.02.1998), columns 5-6.	1-3, 8
A	US 5,360,779 A (CHEUNG et al) 01 November 1994 (01.11.1994), columns 1-2.	1-9

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

\* Special categories of cited documents:

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